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Efficient adsorbent based on bentonite functionalized with 3-aminopropyltriethoxysilane for dyes removal from aqueous solutions

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The present work focuses on intercalating a natural bentonite with an organo-inorganic specieobtained by hydrolysis of 3-aminopropyltrimethoxysilane in order to improve its adsorption capacity. The material obtained is used in the deppolution of water polluted by dyes. Methylene blue is chosen as a model pollutant. In order to be able to characterize this clay after modification, we used several physico-chemical and mineralogical analysis techniques such as X-ray diffraction, infrared spectroscopy, chemical and thermal analysis. The cationic exchange capacity was determined as well. In addition, with a view to optimization, the effects of several adsorption factors, including time, pH, dye concentration, and masse of clay on the adsorption capacity of methylene blue by the adsorbent were assessed as well. The results of this study showed that Langmuir isotherm is the model which best characterized the adsorption of methylene blue by the developed adsorbent (Bent-APTES) with a capacity of 217.40 mg g^{-1}.Accordingly, the modified Algerian bentonite may be utilized as a potential adsorbent for the treatment of waste effluents polluted by cationic dyes from wastewaters.

KEYWORDS

Bentonite; 3-aminopropyltrimethoxysilane; adsorption; methylene blue.

Introduction

Attention to the environment and its issues in recent years has been the focus of many researchers in various fields [1-4].

It is widely admitted that over the last few decades, the development of human society has been growing rapidly, leading to the use of a large number of hazardous dyes that are considered as the most worrying sources of pollution [5]. No one denies that the presence of dyes in water, even at low concentrations, is highly poisonous to all living creatures and ecosystems [6,7].

It is worth indicating that methylene blue (MB) is a water-soluble cationic dye with high chromaticity; it is extensively utilized as a chemical indicator, bacteriologic stain, biological stain, coloring agent, and the like. In this context, Russo*et al.* [8] found out that methylene blue (MB) is quite visible and stable in water at room temperature. In addition, as this synthetic dye is extensively employed in various areas, including paper, food processing, plastics, printing and others, which are closely associated with our daily life, it has become extremely urgent to develop efficient ways to remove this dye

from wastewaters. Therefore, several methods such as flocculation, coagulation, membrane filtration, adsorption and some electrochemical methods have been conceived and developed so far for the purpose of extracting and eliminating dyes from effluents [9-11]. Many researchers have revealed that adsorption is one of the most effective chemical engineering processes used for the effective elimination of industrial wastewater pollutants, such as dyes, from wastewater effluents [12-13].

It is widely acknowledged that clay minerals are widely spread in our environment; they are low cost and environmentally friendly materials that have turned out to be highly efficient in environmental remediation which involves removing pollutants or contaminants from environmental media like soil, air, groundwater, or surface water [14].

The clay sheets have a deficit of charge as a result of isomorphic substitutions (for example Al^{3+} replaced by Mg^{2+} or Fe^{2+} in the octahedral sheet, Si^{4+} replaced by Al^{3+} in the tetrahedral sheet). Note that this substitution is the main source of negative and positive charges in clay minerals [15].

Bentonite is a material that is frequently employed in developing nanocomposites and eco-friendly materials due to its good aspect ratio [16-18], high swelling capacity [19] and ion exchange capacity [20].

Several studies have reported that a number of adsorbents can be modified in order to enhance their adsorption capacities [21].

On the other hand, many researchers showed that silylation is an effective technique for clay minerals modifications [22-25].

Furthermore, it has been mentioned that clays modified by organosilanes prevent secondary pollution which may result from leaching of the intercalated surfactant into surrounding solutions when organoclays are used as adsorbents [26-27]. Thus, pillaring clay materials with oligosilsesquioxane species represent a new class of sorbents for effective polluant removal from wastewater where their preparation is relatively inexpensive and easy compared with that of other modifications of bentonite.

Several research groups have focused on the improvement of Algerian clay, showing never or very seldom was modified by the molecule 3-aminopropyltriethoxysilane.
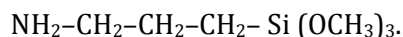
The main objective of this research was to investigate the ability of an Algerian bentonite, which was previously modified by the silylation procedure, and to evaluate its possible usage in the removal of methylene blue (MB) from effluents. For this, it was deemed important to assess various operational parameters. Then, several models of adsorption isotherms were used. Furthermore, the characterization of the modified bentonite was carried out.

Materials and methods

Materials

The Algerian bentonite (Bent) used in this study was a montmorillonite, a claymineral of the smectite group having silicate trahedral sheets layered between alumina octahedral sheets.

It was brought from a quarry in the region of Maghnia, a town in the northwestern part Algeria. As for the silane used in this research, it is 3-aminopropyltriethoxysilane (APTES). Its chemical formula is

$NH_2–CH_2–CH_2–CH_2– Si (OCH_3)_3$.

Physical-chemical characterization methods

X-ray diffraction analyses of bentonite before and after modification samples were performed using a D8-Advance diffractometer with monochromatic $CuK\alpha1$.

Fourier transform infrared spectra were obtained by the KBr pellet method using a Perkin Elmer 1600.

The chemical composition of the samples was determined through X-ray fluorescence spectrophotometer. In addition, the thermogravimetry-differential thermal analysis (TG-DTA) measurements were performed in air by means of a Perkin Elmer Pyris DTA-TGA analyzer.
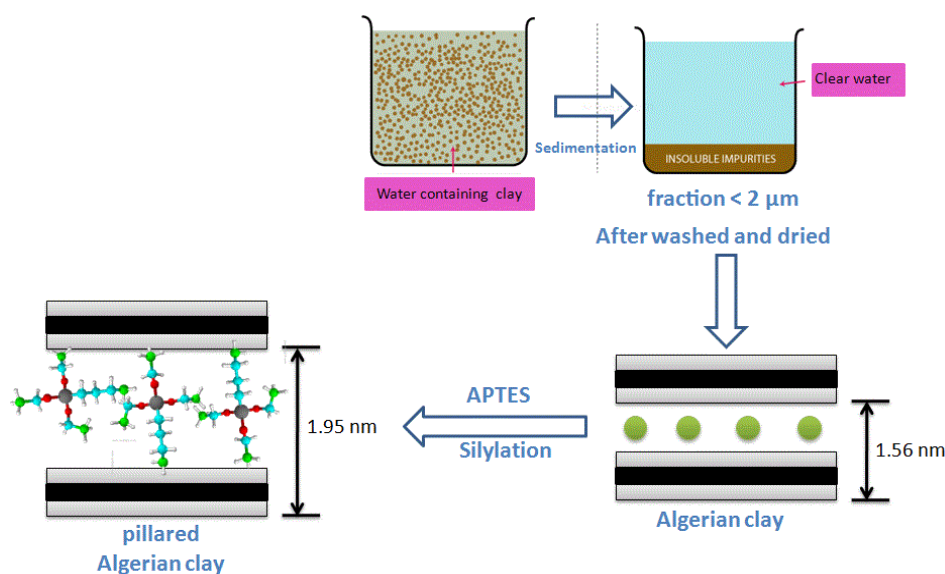
Preparation of pillared clay

The pillared clay (Bent-APTES) was prepared by first sedimenting the bentonite in order to eliminate the size fraction that was superior to 2µm. The resulting material was then named Bent.

On the other hand, the preparation of pillaring solutions was conducted in the following way.

First, the quantities of 20 g of 3-aminopropyltrimethoxysilane and 60 mL of methanol were mixed and kept under stirring for a given period, at room temperature. Next,

6 mL of HCl (16%) was included in a drop wise manner. After this, the mixture obtained was agitated again for 27 hours. Afterwards, the mixture was heated under reflux for one hour after adding 300 mL of acetone. The last step consisted of cooling the mixture down to room temperature, while keeping it under stirring for 3 h. The resulting solution was then stored in the dark for 2 hours. During this process, the condensation of silanes generally led to the formation of polysiloxanes.

Furthermore, the intercalated bentonite was obtained by adding slowly the pillaring solution (4 mL/min) to the sedimented bentonite in suspension dropwise, at the rate of 5 g in 1670 mL of deionized water [28]. Next, the modified bentonite was centrifuged, washed with deionized water (2 L/g), and was then subjected to thin-layer drying in air. The sample obtained was referred to as Bent-APTES, as illustrated in Scheme 1.

Scheme 1 Silylation of Algerian bentonite with APTES

Determination of the cation exchange capacity

The conductimetric method, which has widely been described in previous works, was utilized to estimate the cation exchange capacity (CEC) [29-30].

Adsorption studies

Adsorbate and other chemicals

Methylene blue was employed as a model pollutant. Its molecular formula is $C_{16}H_{18}ClN_3S$ and its molecular weight is equal to 319.851 g/mol.

A stock solution containing 1 g/L of MB was prepared by deionized water and then diluted to the desired concentration to be used in each experiment. In addition, a UV/Vis (V-670) was used to determine the concentration at the wavelength 665 nm. HCl and NaOH were employed to adjuste the pH of the solution.

Adsorption experiments

The experimental variables examined were the contact time, bentonite concentration in suspension, pH and MB concentration. These experiments were conducted following the steps below. First, the quantity of 0.5 g of dry adsorbent Bent-APTES was mixed to 100 mL of MB at a given concentration. This solution was then magnetically mingled at a distinct time period (0–140 min) at room temperature.

The supernatants were analyzed by UV spectrophotometer in order to determine the amount of methylene blue adsorbed. The adsorption experiments in this study were effectuated within the initial pH range, i.e. between 2 and 11. Moreover, the influence of the amount of adsorbent on MB removal was investigated by raising the quantity of adsorbent from 0.25 g to 4.0 g. For the purpose of determining the adsorption isotherms, the present study was conducted with various initial concentrations of methylene blue varying from 5 mg/L to 340 mg/L.

The MB uptakes were estimated using the equations given below:

$$q_t = (C_0 - C_t)\frac{V}{m} \tag{1}$$

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{2}$$

q_t and q_e (mg/g) per unit mass of clay adsorbent at time t and at equilibrium, are the concentrations of the MB in the initial solution (mg/L) and after sorption, respectively. C_0, C_t and C_e (mg L^{-1}) are the concentrations of MB solution at the initial time, at time t and at equilibrium after sorption, respectively; V (L) is the volume of the aqueous phase and m (g) represents the amount of bentonite.

Results and discussion

Adsorbent characterization

Chemical analysis reported in Table 1 shows that the silicon and oxygen contents increased, while calcium, sodium and potassium completely disappeared for the Bent-APTES intercalated clay. These results confirm the occurrence of the cation exchange process (Na$^+$, Ca^{2+}, K$^+$) for the organosilicon oligomer species.

The X-ray spectra of natural and modified clay are illustrated in Figure 1. Note that the basal spacing for natural clay (Bent) is equal to 1.56 nm.

TABLE 1 Chemical composition (mol% of oxides) of Bent and Bent-APTES

Materials	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	Na$_2$O	K$_2$O
Bent	44.42	14.65	2.83	0.77	3.43	4.05	1.92
Bent-APTES	81.92	17.07	2.27	0.00	2.78	0.00	0.00

After silylation, that value increased to 1.95 nm, which means that silane entered in the Bent galleries [27-28,31]. In addition, the new reflection observed at around 2θ=8° is certainly due to the (002) reflection of the silylated product [20,2]. According to some studies previously conducted by Chen *et al.* [32], the phyllosilicate sheet thickness and the basal spacing were used to determine the height of the phyllosilicate sheet which is estimated to be 0.96 nm. This result indicates that the value obtained is large enough to accommodate the 3-aminopropyltrimethoxysilane molecule. In

addition, it is clearly seen that the full width at half maximum (FWHM = 0.503) of the (d_{001}) peak for the modified bentonite (Bent-APES) has slightly declined after silylation in comparison to that of natural bentonite (FWHM = 0.349). This could be explained by the slight decrease in the ordered clay sheets. However, despite this decrease, the two-dimensional structure of bentonite was preserved.

Furthermore, the XRD analysis of modified bentonite clearly indicated that the APTES pillaring on the bentonite surface was successfully achieved.

The IR spectra of unmodified bentonite (Bent) and silylated bentonite (Bent-APTES) are shown in Figure 2.

FIGURE 1 X-ray diffraction patterns of Bent and Bent-APTMS

The band at about 3625 cm^{-1} corresponds to stretching vibrations of hydroxyl groups of the structural -OH groups in Bent. In addition, the broad bands in the region between 3000 cm^{-1} and 3600 cm^{-1} and around 1630 cm^{-1} are due to the vibrations of the adsorbed water [14]. Moreover, the strong absorption band situated near 1000 cm^{-1} is assigned to the Si-O-Si stretching vibrations.

After silylation, the FTIR spectrum shows new bands. According to Vashist *et al.* [33],

the peaks at 1132 and 1194 cm^{-1} are characteristics of Si−OCH$_2$CH$_3$. In addition, the absorption bands near 2932 and 2852 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of methylene-CH$_2$-, respectively [30,31]. Further, the band situated around 3370 cm^{-1} and the shoulder located at ~3290 cm^{-1} may be assigned to the stretching vibrations of the -NH$_2$ group [31,32].
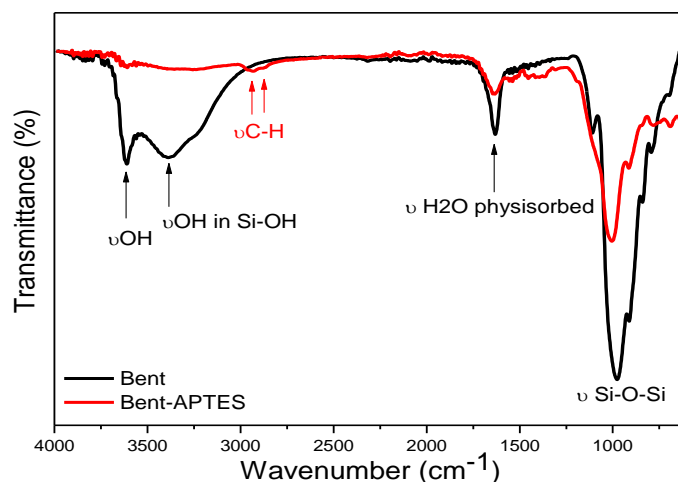
FIGURE 2 Comparison IR spectrum of unmodified bentonite (Bent) and silylated bentonite (Bent-APTES)

The thermograms (TG) and derivative thermograms (DTG) of Bent and Bent-APTES are depicted in Figure 3. It should be noted that the thermogravimetric analysis of natural bentonite shows two distinct regions corresponding to two different temperature ranges, i.e. [56-110] °C and [480-510] °C. They are mainly attributed to the loss of the physically adsorbed water and to bentonite dehydroxylation [37]. On the other hand, the decomposition of modified bentonite (Bent-APTES) exhibits six steps, as shown on the DTG curve. The peak around 100 °C is attributed to the loss of the physically adsorbed water [34], while those in the region from 225 to 580 °C are assigned to the decomposition of the intercalated chemically bonded silane [27]. It is also observed that after the silylation of bentonite, the DTG curve indicates that the temperature of 750 °C corresponds to the dehydroxylation process. It was revealed that the silylation of bentonite increases the thermal stability of Bentonite.

Cation exchange capacity

It was found that Bent-APTES has a cation exchange capacity (CEC) of the order of 31.03 meq/100g of clay. This CEC value is significantly lower than that of the original clay (89.86 meq/100g). This decrease can certainly be explained by the fact that the organosilicon oligomer, which was initially fixed as a compensating cation, occupies the exchange sites of the interlamellar space of bentonite.

As confirmed by the XRD, FTIR, TGA and SEM analyses of modified bentonite, the APTES pillaring on the bentonite surface was successfully achieved.
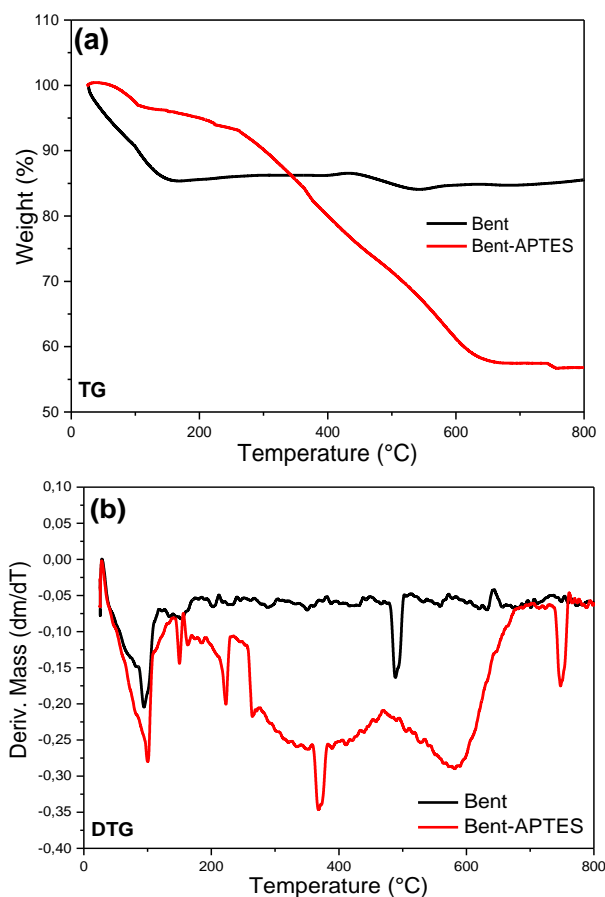
FIGURE 3 TG (a) and DTG (b) curves of natural bentonite (Bent) and modified bentonite (Bent-APTES)

Adsorption

Kinetic study of MB adsorption

The kinetic process gives fundamental information about the the influence of contact time up on the polluant retention. The evaluation of the adsorption uptake of MB onto Bent-APTES is presented in Figure 4. It was found that the adsorption of MB was faster during the initial period (5 min) and then it became very slow during the next 10 minutes. The rapid increase in the amount of adsorbed dye at the beginning of the process could be attributed to all sites on the adsorbent surface which were vacant. The equilibrium time was realized after 15 min.
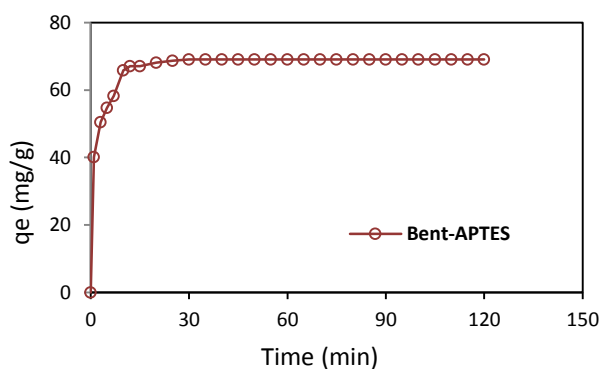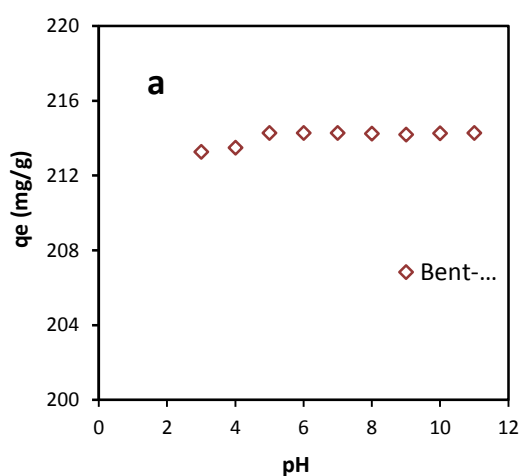

FIGURE 4 The kinetic of MB removal by the Bent-APTES adsorbent

Effect of pH

The influence of the initial pH on removal of methylene bleue using Bent-APTES was examined for different pH values within the interval [3–11], while fixing the other parameters, as illustrated in Figure 5a, showing that the uptake (q_e) of methylene blue (MB) by Bent-APTES was not significantly affected by the pH due to the buffering effect of the adsorbent. Similar results about the effect of pH on the organic cation adsorption are available in the literature. For instance, Narine *et al.* [38] indicated that the adsorption capacity of bentonite for dye removal was unchanged over the pH range [4.5-8.5]. Furthermore, similar observations reported by other authors tendencies were for the cationic dye removal by bentonite montmorillonite, palygorskite, and sepiolite[39-41].

Effect of Bent-APTES*dosage on MB removal*

It was established that in order to achieve the optimal cost removal of polluants from wastewaters, the right amount of adsorbent was required to achieve optimum performance. Figure 5b shows clearly the effect of different Bent-APTES dosages on the removal of MB, over a period of 30 min of contact time.

Figure 5b suggests that when the adsorbent dosage passes from 0.5 to 1 g L^{-1}, the amount of adsorbed MB rises. This is most likely attributed to the presence of active adsorption sites on the adsorbent surface, which facilitates the adsorption operation. It is also worth indicating that although higher Bent-APTES dosages provided highly efficient removal of methylene blue (MB), successive increases in Bent-APTES dosage to above 1g L^{-1} did not make the elimination of MB. Consequently, it can be deduced that the optimal concentration of Bent-APTES adsorbent of MB removal from wastewaters is 1g L^{-1}.
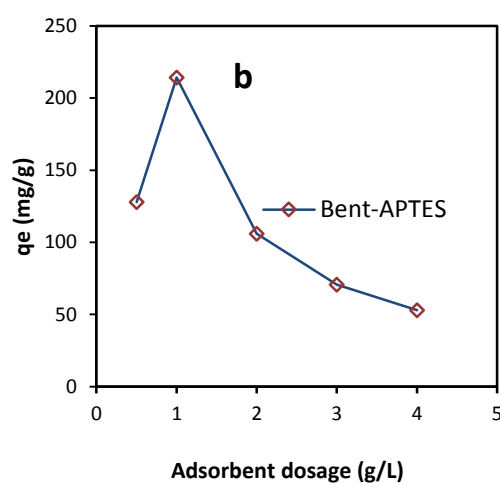

FIGURE 5 Effects of pH (a), and Bent-APTES adsorbent dosage (b) on MB removal

Isotherm models

In this section, the sorption behavior of MB onto Bent-APTES adsorbent is assessed. In this context, two theoretical models, namely Freundlich isotherm model [42] and Langmuir isotherm model [43], were selected and tested to fit the recorded data.

Langmuir's model involves single-layered adsorption on a surface containing individual fixed sites. These binding sites have uniform adsorption energy. The linear form of the Langmuir isotherm is represented by the following Equation (3):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{3}$$

where q_e (mg/g) is the dye amount in milligrams adsorbed per gram of bentonite, from the aqueous solution, C_e (mg/L) is the equilibrium concentration of dye ions in the aqueous solution, K_L is the Langmuir equilibrium constant and q_m (mg/g) is the maximum adsorption capacity. Note that q_e and C_e may be deduced from the slope and intercept of the Langmuir linearized plot (Ce/qevs. Ce), as illustrated in Figure 6a.

The Freundlich adsorption model is used when more than one adsorption monolayer may form on the surface of solid and the sites are heterogeneous with different binding energies. The linear form of the Freundlich isotherm is given by the following Equation (4):

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \qquad (4)$$

Where q_e (mg/g) is the dye amount in milligrams adsorbed per gram of bentonite, from the aqueous solution, C_e (mg/l) is the concentration of dye in the aqueous solution at equilibrium, n and K_F are the Freundlich constants.

The graphical representation (Figure 6b) of $\log q_e$ vs. $\log C_e$ leads to regression lines from which the theoretical Freundlich values n and K_F are calculated.
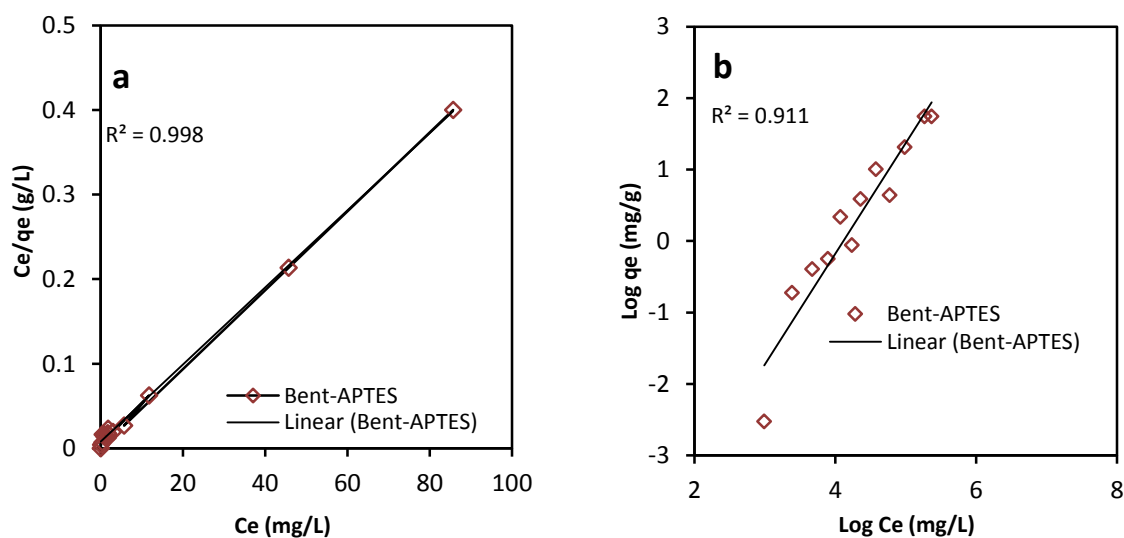
The experimental data were fitted to the two aforementioned models. The adjustable parameters and coefficient of determination (R^2) obtained are listed in Table 2.

The calculated and experimental amounts of the maximum adsorption capacity (q_m) were found equal to 217.40 and 214.280 mg g^{-1}, respectively.

Based to the data displayed in Table 2, the Langmuir model gives a better regression coefficient ($R^2 > 0.99$) in comparison to that of the Freundlich isotherm model (Table 2). These data clearly indicate that MB was adsorbed on Bent-APTES *via* monolayer adsorption.

Comparison of bent-APTES against various adsorbents

The adsorption performance towards methylene blue dye and other adsorbents reported in the literature are shown in Table 3. The maximum adsorption capacities of MB obtained in this study are considered reasonable compared with other adsorbents. Therefore, one may confidently conclude that the Bent-APTES adsorbent has considerable potential for the treatment of waste effluents polluted by dyes.

FIGURE 6 (a) Langmuir, and (b) Freundlich isotherms models, for the adsorption of MB onto Bent-APTES

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TABLE 2 Parameters of the Langmuir and the Freundlich isotherms for MB adsorption onto Bent-APTES

	Langmuir isotherm model			Freundlich isotherm model		
Adsorbate	q_m (mg/g)	K_L (L/mg)	R^2	n	K_f (mg/g)	R^2
MB	217.400	0.657	0.998	1.549	0.0017	0.911

Conclusion

This study attempted to use 3-aminopropyltriethoxysilane to functionalize bentonite clay in order to remove methylene blue from aqueous solutions. The recorded characterization data suggested significant differences between functionalized and non-functionalized bentonite, which suggests that the intercalation process was successfully achieved. Furthermore, the modified clay exhibited high capacity for the removal of methylene blue (MB) from wastewater. In addition, the effects of parameters such as the contact time, initial dye concentration, pH value, and adsorbent mass on the adsorption process were analyzed and discussed. Moreover, the uptake of MB from the aqueous solution by Bent-APTES occurred via monolayer adsorption, which could well be described by the Langmuir isotherm model. The Bent-APTES might be a promising adsorbent for the selective removal of dyes from wastewaters.

These results prove that the design and production of new adsorbents with natural low cost material are becoming very interesting and are beginning to find utilizations in the fields of environmentology.

Acknowledgements

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